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Anthropogenic Influence on Atmospheric Oxidants and the Sulfur Budget

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ABSTRACT

We use a global chemical transport model constrained by observations of ice cure sulfate oxygen isotopes to simulate anthropogenic impacts on oxidant (OH, O_3, H_2O_2) and sulfur budgets. The Arctic ice core sulfate oxygen isotope observations are insensitive to changes in oxidant concentrations on the preindustrial-industrial timescale due to the rising importance of metal catalyzed S(IV) oxidation in mid- to high-northern latitudes resulting from anthropogenic metal emissions. The small change in Antarctic ice core sulfate O-isotope observations on this timescale are consistent with simultaneous increases in boundary layer O_3 (32%) and H_2O_2 (49%) concentrations in the southern hemisphere, which have opposing effects on the sulfate O-isotope anomaly. Despite large changes in global oxidant abundances and sulfur emissions since preindustrial times, the relative importance of gas- versus aqueous-phase sulfate formation has remained constant.

I. INTRODUCTION

The oxidation capacity of the atmosphere (usually defined by global mean OH abundance) has large implications for GHG (e.g. CH_4) and pollutant (e.g. CO) concentrations. Little to no information exists on how oxidant abundances have varied in the past. Hence we rely on models; however, modeled changes in OH and O_3 in the past show disagreement among different studies due to large uncertainties in emissions of O_3 precursors.

The $\Delta^{17}O$ value of sulfate and nitrate from ice cores currently provides the most promising proxy for paleo oxidant concentrations. The $\Delta^{17}O$ value of sulfate is a function of the relative importance of its various oxidation pathways, which is in large part determined by atmospheric oxidant abundance (in addition to pH and liquid water content of clouds). It can also be used as an indicator of the relative importance of gas- versus aqueous-phase sulfate formation, which has implications for the direct and indirect forcing of sulfate aerosol.
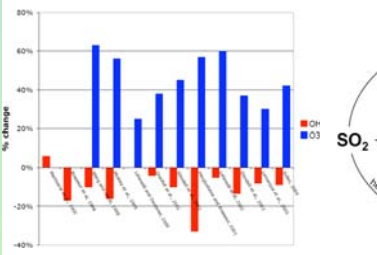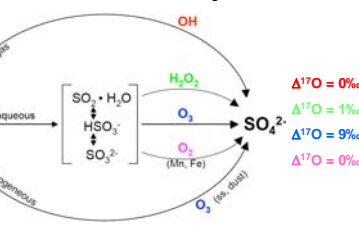

Figure 1. Modeled percent change in annual-mean tropospheric OH and O_3 concentrations in the present day relative to the preindustrial from different studies.

Figure 2. S(IV) oxidation pathways and their corresponding $\Delta^{17}O(SO_4^{2-})$ values ($\Delta^{17}O = \delta^{17}O - 0.5 \times \delta^{18}O$) [Savarino et al., 2000].

II. ICE CORE OBSERVATIONS

Arctic $\Delta^{17}O(SO_4^{2-})$ ice core and aerosol observations show an unexpected decrease throughout the industrial period. This decrease is unexpected due to known increases in O_3 concentrations over this time period.
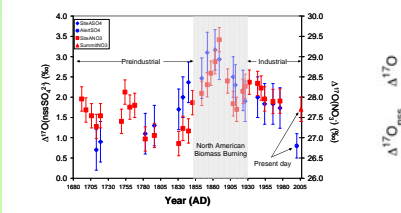
Antarctic $\Delta^{17}O(SO_4^{2-})$ ice core observations show a small increase from the mid- to late-1700s leveling off in the mid- to late-1800s. The timing of the increase is coincident with increases in southern hemisphere biomass burning [Marlon et al., 2008].
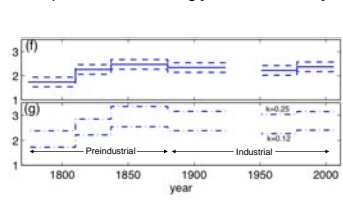

Figure 3. $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(nitrate)$ since 1680 A.D. from Greenland ice core and snowpit and Arctic aerosol observations (produced using data from Alexander et al. [2004], McCabe et al. [2006] and Kunasek et al. [2008]).

Figure 4. Raw $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(nssSO_4^{2-})$ since 1770 A.D. from the West Antarctic Ice Sheet (WAIS) Divide ice core (Figure 2 from Kunasek et al., manuscript in prep). Note: k values represent different assumptions regarding the SO_4^{2-}/Na^+ ratio in sea-water.

III. METHODS

We use the GEOS-Chem model [Bey et al., 2001], a global 3D chemical transport model driven by assimilated meteorology at 4°x5° horizontal resolution and 30 sigma vertical levels, to simulate oxidant concentrations and $\Delta^{17}O(SO_4^{2-})$ in the present day and preindustrial time periods.

Table 1. GEOS-Chem model configuration for the preindustrial and present day.

Model Configuration	Preindustrial	Industrial
Meteorology	GEOS-4 1989-1991	GEOS-4 1989-1991
Fossil Fuel Emissions	OFF	GEIA
Fertilizer Emissions	OFF	GEIA
Biomass Burning Emissions	scaled to 10% of industrial	Duncan et al./GFED2
Biogenic Emissions	GEIA/MEGAN	GEIA/MEGAN
Biofuel Emissions	GEIA	GEIA
CO_2	285 ppmv	355 ppmv
CH_4	792 ppbv	1700 ppbv

IV. MODEL RESULTS

Calculated global mean changes in tropospheric OH (-9%), O_3 (+42%) and H_2O_2 (+58%) in the present day relative to the preindustrial are consistent with previous modeling studies (see also Figure 1).
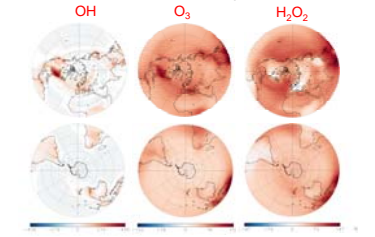

Figure 5. Percent change in boundary layer oxidant concentrations in the present day relative to the preindustrial

The fraction of sulfate formed in the gas-phase, important for direct and indirect radiative forcing of sulfate aerosols, does not change despite large changes in the sulfur and oxidant budgets.

Table 2. Calculated sulfur budget in the present day and preindustrial.

	Preindustrial	Present day
Sulfur Emissions (Tg yr⁻¹)	23.6	92.0
Sulfur Burden (Tg)	0.42	0.97
Fraction of sulfate formed via gas-phase SO_2 + OH	23%	26%

Impact of oxidant changes on $\Delta^{17}O(SO_4^{2-})$ and comparison with ice core observations

Table 3. Change (‰) in $\Delta^{17}O(SO_4^{2-})$ in the present day relative to the preindustrial. Measurement uncertainty in the observations is ±0.3‰.

	Model (base[a])	Model (with metal catalyzed S(IV) oxidation)	Ice core observations
Arctic (Greenland[b] and Alert[c])	+0.2	-0.7	-0.7±0.4[d]
Antarctic (WAIS[d])	+0.2	+0.2	+0.2±0.5[e]

[a]base scenario includes S(IV) oxidation by OH, H_2O_2 and O_3
[b]Alexander et al. [2004] (see Figure 3)
[c]McCabe et al. [2006] (see Figure 3)
[d]Kunasek et al., manuscript in prep.(see Figure 4)
[e]error represents the 1σ standard deviation of the preindustrial observations

Sulfate formed via metal catalyzed oxidation is dominated by anthropogenic metal emissions in mid- to high-northern latitudes in the present day, and represents up to ~half of (annual mean) total sulfate formation.
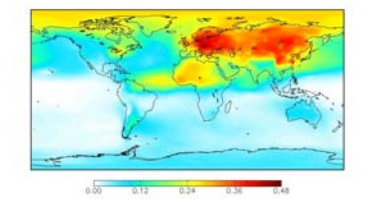
Figure 6. Annual mean fraction of total sulfate at the surface formed via metal catalyzed oxidation (Figure 4 from Alexander et al. [2009]).

V. CONCLUSIONS

• A decrease in modeled $\Delta^{17}O(SO_4^{2-})$ (-0.7‰) in Greenland in the present day relative to the preindustrial is consistent with the Greenland ice core record (-0.7±0.4‰) [Alexander et al., 2004]. The unexpected decrease in $\Delta^{17}O(SO_4^{2-})$ on this timescale is explained by the rising dominance of metal catalyzed S(IV) oxidation from anthropogenic metal emissions, despite large increases in O_3 concentrations (50%) in the northern hemisphere.

• A small decrease in modeled $\Delta^{17}O(SO_4^{2-})$ (-0.2‰) in Antarctica in the present day relative to the preindustrial is consistent with a small change in the Antarctic observations (+0.2±0.5‰) [Kunasek et al., manuscript in prep.]. The lack of a significant change in Antarctic $\Delta^{17}O(SO_4^{2-})$ on this timescale is consistent with simultaneous increases in O_3 (32%) and H_2O_2 (49%) concentrations in the southern hemisphere which have opposing effects on $\Delta^{17}O(SO_4^{2-})$.

VI. FUTURE DIRECTIONS

$\Delta^{17}O(SO_4^{2-})$ from the Vostok ice core shows large (3.5‰) changes on the glacial-interglacial timescale, consistent with increased OH (and CH_4 sink) during the last glacial.
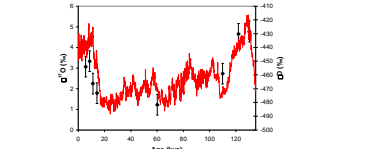

Figure 7. $\Delta^{17}O(SO_4^{2-})$ and δD over a full glacial-interglacial cycle from the Vostok ice core (Figure 1 from Alexander et al. [2002]).

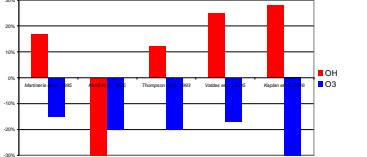Modeled changes in OH and O_3 in the LGM relative to the preindustrial show large disagreement among different studies.

Figure 8. Modeled percent change in global-mean tropospheric OH and O_3 concentrations in the LGM relative to the P.I.

In collaboration with Loretta Mickley, Gavin Schmidt, Jed Kaplan and others, we are simulating oxidant concentrations and $\Delta^{17}O(SO_4^{2-})$ on the glacial-interglacial timescale using an offline coupling between GEOS-Chem (CTM), GISS ModelE (GCM), and BIOME-4 (global terrestrial vegetation model). We are testing the sensitivity of $\Delta^{17}O(SO_4^{2-})$ to changes in oxidants on this timescale in order to provide an observational constraint for oxidant concentrations in the past.

ACKNOWLEDGMENTS

REFERENCES

Alexander, B., Savarino, J., Barkov, N. I., Delmas, R. J., and Thiemens, M. H.: Climate driven changes in the oxidation pathways of atmospheric sulfur, Geophys. Res. Lett., 29, 10.1029/2002GL014879, 2002.; and other references.